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Catalytic gasification of algae *Nannochloropsis sp.* in sub/supercritical water

Qingqing Guan[a,b,*], Chaohai Wei[b], Ping Ning[a], Senlin tian[a], Junjie Gu[a]

[a]*Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China.*
[b]*The Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions, South China University of Technology, Guangzhou 510006, China*

Abstract

Gasification of *Nannochloropsis sp.* in sub/supercritical water with NaOH, KOH, Pd/C and Ru/C was investigated. The results showed the yields of H_2 and CH_4 were dramatically improved by NaOH, KOH, Ru/C and Pd/C. Gasification of Ethylbenzene indicated those catalysts can enhance gasification of recalcitrant intermediate products which led to an efficient gasification of algae. It's also found that the presence in algae of sulfur could present challenges for gasification of algae with Ru. As cleavages of aromatic ring were observed with NaOH and KOH, we speculated hydroxide could form OH radicals and OH addition to aromatic ring causes the ring-opening.

Keywords: Gasification; Algae; Sub/Supercritical water; Catalysis; Ru

1. Introduction

The environment and energy became the most concerned issue in this century. As algae grow faster than lignocellulosic biomass, there is an increasing interest in using microalgae to make biofuels [1]. Gasification is a way to produce fuel gases containing H_2, CH_4, and CO [2]. Algae are high-moisture biomass, which makes them difficult to be gasified for conventional technologies as vaporization of the water is needed. Moreover, water vapor to remove moisture from alga leads energy-consumption, which means offsetting some of the energy gained by producing the gaseous products.

It was reported that biomass can be rapidly gasified in sub/supercritical water (SCW) [3] since the mass transfer rates are dramatically increased [4]. The process of supercritical water gasification (SCWG) does not require a dry feedstock, so it is suitable for gasifying algae. Moreover, SCWG can lead to low

* Corresponding author. Tel.: +86-0871-5170905.
E-mail address: qingqing_guan2000@yahoo.com.cn.

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tar and char formation and high hydrogen yields as water serves as both reaction medium and reactant of reforming [5].

There have been a few previous studies of SCWG that deal with gasification of algae [6-8]. Recently, we reported SCWG of *Nannochloropsis sp.*, a marine microalga, in the absence of added catalysts and the kinetics. The results indicated that SCWG of microalgae leads to a low gasification efficiency without catalysis unless high temperatures (– 600°C) are used [9, 10]. However, gasification at a lower temperature certainly leads a lower operating cost. Therefore, it's necessary to develop efficient ways to gasify microalgae at a lower temperature.

Catalyzed SCWG is one way to improve gasification efficiency at a lower temperature. Herein we report that catalytic SCWG of *Nannochloropsis sp.* in sub/supercritical water. A comparative study of two homogeneous catalysts (NaOH and KOH) and two heterogeneous catalysts (Ru/C and Pd/C) were preformed firstly, then, the mechanism of SCWG of algae was discussed. In this work, we also highlight the potential difficulties and challenges of gasification of algae with heterogeneous catalysts.

2. Materials and methods

We purchased Microalga (*Nannochloropsis sp.*) paste from Reed Mariculture (*Nannochloropsis 3600*). Chemicals were purchased from Fisher Scientific. 316-stainless steel mini-batch reactors were used for gasification experiments, which were depicted in details in our previous works [9, 10]. Reactions were carried out by placing the reactors vertically in a Techne Fluidized Sand Bath (model SBL-2). In a typical process, microalgae paste was loaded into a reactor and then deionized water was added. After the desired reaction time, the reactors were removed from the sand bath and cooled. The gaseous products were analyzed by an Agilent Technologies model 6890N gas chromatograph (GC) with a thermal conductivity detector (TCD). The catalysts were characterized by a JEOL-2010F scanning transmission electron microscope (STEM) with an energy dispersive spectroscopy (EDS) detector.

3. Results and discussion

Under the conditions that at 40 min, 450 °C, with water density 0.087 g/cm^3, 4.7 wt% loading and 1 g/g catalyst loading, the gaseous products from catalytic SCWG of *Nannochloropsis sp.* with NaOH, KOH, Pd/C and Ru/C are shown in Fig. 1. Clearly, the yields of gaseous products H_2 and CH_4 were dramatically improved by 4 catalysts, especially with Ru/C. Only 2.4 mmol/g H_2 and 0.95 mmol/g CH_4 were produced by direct gasification of algae while 16.3 mmol/g H_2 and 5.1 mmol/g CH_4 were gained by SCWG with Ru/C, which indicated Ru/C can enhance the gasification of algae in supercritical water at a lower temperature. Pd/C, KOH and NaOH also increased gasification of algae. But it should be noted that the yield of CO_2 was decreased by NaOH and KOH, which also observed by Muangrat et al as NaOH and KOH capture CO_2 to form metal carbonates [11].

Our previous research [9] showed that alga decomposes to form two types of non-gaseous intermediate products, which then react further to form either char or gases. One class of intermediate products comprises aromatic compounds such as Ethylbenzene, which were the most abundant product and are difficult to be gasified. To assess the efficacy of gasifying these recalcitrant compounds, we did experiments with gasification of Ethylbenzene. Fig. 2 shows that Ethylbenzene was gasified efficiently, which indicates that recalcitrant intermediates can be converted to gases with catalysts NaOH, KOH, Pd/C and Ru/C. Therefore, it might be that those catalysts can enhance the SCWG of recalcitrant intermediate products which leads to efficient gasification of algae.

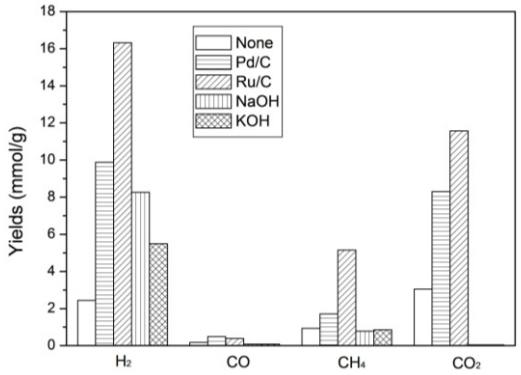


Fig. 1. Catalytic SCWG of algae with 1 g/g catalysts at 450 °C, 40 min, water density 0.09 g/cm^3 and 4.8 wt% loading.

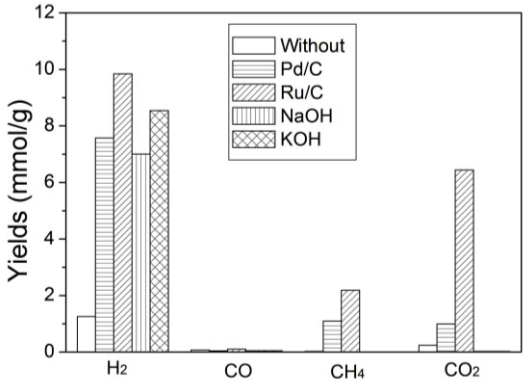


Fig. 2. Catalytic SCWG of Ethylbenzene with 1 g/g catalysts at 450 °C, 40 min, water density 0.09 g/cm^3 and 4.8 wt% loading.

Ru/C is the most efficient one of catalysts tested. In Fig. 3, the gasification efficiency was shown with the Ru/C catalyst after its original, second, and third at 410 °C, with a water density of 0.09 g/ cm^3, 4.8wt%. The results indicated that the gasification efficiency decreased with repeated use and the gasification efficiency obtained with the thrice-used catalysts represents the extent of non-catalytic SCWG. Thus, the thrice-used Ru/C catalyst is likely inactive.

STEM was used to characterize the morphology of the Ru/C catalyst. Fig. 4 shows that most of the Ru particles had increased from 3.9 to about 5 nm after the third use. These physical effects might be responsible for some small portion of the catalyst deactivation. The physical changes alone, however, are probably not primarily responsible for the activity loss as Osada et al. showed that a 100% gasification efficiency can be achieved with used catalyst if given a sufficiently long time [12]. But in this case, a longer time does not increase the gas yield from the thrice-used catalyst.

Energy dispersive spectroscopy (EDS) was used to determine the composition of the Ru/C catalyst after use. The results showed that a peak for sulfur was found along with the peaks of ruthenium and carbon. As sulfur is well known as a poison for Ru, sulfur is probably a chief contributor to the deactivation of catalysts. Therefore, the presence in algae of sulfur could present challenges for gasification of algae with metal catalysts.

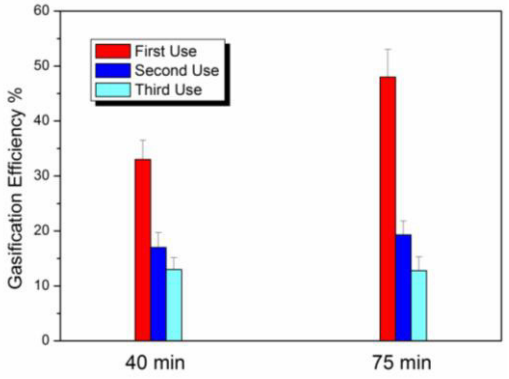


Fig. 3. Gasification efficiency of Ru/C reuse (410 °C, 40 min, 4.8 wt% algae loading, 0.09 g/cm^3 water density, Ru/C 1 g/g).

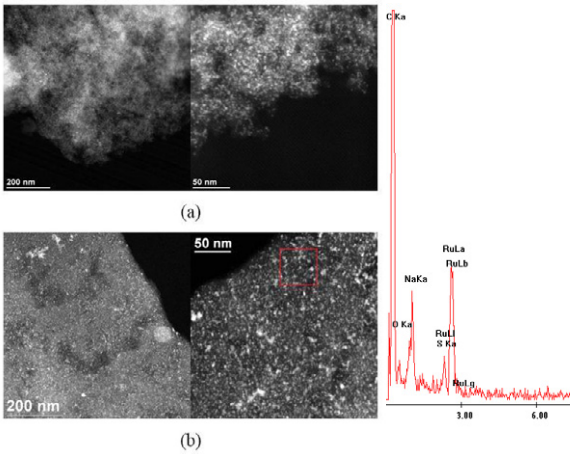
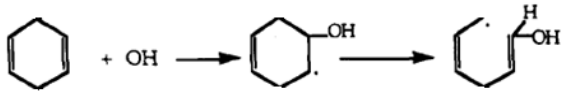


Fig. 4. STEM figures of (a) before use, (b) after third use and EDS results.

Homogeneous catalysts NaOH and KOH were also observed dramatic improvement of the yields of fuel gases. The mechanism generally accepted was explained by action of water-gas shift reaction with alkali [13]. Yoshida and Oshima's work [14] showed that the cleavages of aromatic ring hardly occur at the temperature around 400 ^{o}C and our work also showed that aromatic ring was difficult to be gasified at a higher temperature around 450 ^{o}C [15]. In this case, it's observed that alkali served as ring-breaking reactant for Ethylbenzene's gasification. Therefore, we speculated that hydroxide could form OH radicals in supercritical water and OH addition to aromatic ring causes the ring-opening process, which might be the reason of efficient gasification of algae with alkali catalysts.



4. Conclusions

As the yields of gaseous products H_2 and CH_4 were dramatically improved by 4 catalysts, the results indicated NaOH, KOH, Pd/C and Ru/C can serve as efficient catalysts for gasification of algae. Ru/C is the most efficient one of catalysts tested, 16.3 mmol/g H_2 and 5.1 mmol/g CH_4 were gained by SCWG at 40 min, 450 °C, water density 0.087 g/cm^3, 4.7 wt% loading and 1 g/g catalyst loading. Experiments done with gasification of Ethylbenzene indicated those catalysts can enhance the SCWG of recalcitrant intermediate products which leads to the efficient gasification of algae. But the gasification efficiency decreased with repeated use with Ru/C. The results of STEM with EDS indicated sulfur caused the deactivation of Ru. We also found that alkali served as ring-breaking reactant for Ethylbenzene's gasification. The mechanism speculated is that hydroxide could form OH radicals in supercritical water and OH addition to aromatic ring causes for the ring-opening process, which might be the reason of efficient gasification of algae with alkali catalysts.

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